Observation of the coherence transition into a collective dense Kondo state by resonant inverse photoemission spectroscopy

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By the resonant inverse photoemission spectroscopy (RIPES), we study the crossover from mixed-valent to heavy-fermion and Kondo regime in CeCoGe$_{1-x}$Si$_x$ (0 ≤ x ≤ 3). We have measured the RIPE spectra as functions of composition and temperature. The strong composition dependence of 4f state ("'f' peak") just above the Fermi level shows that the localized 4f electrons in the compound become itinerant due to the enhanced Kondo effect within the range 1.0 ≤ x ≤ 1.5. Temperature dependence of the f' peak indicates a transition from the paramagnetic state at room temperature to a coherent Fermi-liquid regime at low temperatures where the Kondo effect dominates. The most remarkable variation of the spectra has been observed above 200 K with increasing temperature in CeCoSi$_x$ which has a very high Kondo temperature $T_K$ of about 900 K. This suggests that the change in the 4f-electronic state of CeCoSi$_3$ may be scaled by the coherence transition temperature rather than $T_K$. [S0163-1829(99)0638-3]

Many Ce- or U-based materials show several interesting physical properties, e.g., mixed valence, heavy fermion, superconductivity, and so on. The nature of those systems can be fairly well accounted for by following two competing effects. The first is an on-site Kondo effect that leads to a compensation of the localized moments through the exchange interaction $J$ between the localized 4f-electron and itinerant electrons. The second is the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction that plays an important role in the magnetic ordering in heavy-fermion systems. This is an intersite interaction mediated by the polarized conduction electrons. Both are associated with the same coupling constant $J$. The competition of these two effects generates various phases of the system depending on the magnitude of $J$. The finite-temperature phase diagram for the Kondo lattice has been successfully studied by Doniach in which the renormalized coupling $J = J/W$ ($W$ stands for the bandwidth) is continuously varied. The long-range magnetic ordering emerges below a critical value of parameter $J_c$ as the ground state and the critical line $[T_N(J)]$ exists in the finite-temperature region. In the noncritical region ($J > J_c$), on the other hand, the "coherence transition" from the paramagnetic state to the mixed-valent state in the Kondo lattice has been investigated in Ref. 7 using the scaling theory of critical phenomena. Continentino et al., show that the coherence transition occurs at a temperature, the so-called coherence temperature $T_{coh}$ below the single-impurity Kondo temperature $T_K$ and marks the onset of the collective dense Kondo regime. They have predicted that the $T_{coh}$ has a different dependence on $J$ as compared with $T_K$, especially near the $J_c$.

The nature of the CeCoGe$_{1-x}$Si$_x$ series of compound has been investigated by measuring magnetic susceptibility, electronic resistivity, and specific heat. Substitution of silicon for germanium produces the normal chemical pressure effect which reduces the unit-cell volume by about 10% from CeCoGe$_3$ to CeCoSi$_3$. The coupling constant $J$ is thereby enhanced as the silicon concentration $x$ increases and the antiferromagnetism in CeCoGe$_3$ is suppressed around $x = 1.2$ by the enhanced Kondo effect. The overall behavior of this system is qualitatively understood within Doniach’s magnetic phase diagram. The present system is a good candidate for the investigation of quantum critical behavior in heavy fermion systems. In this work we study the crossover from the coherent Fermi-liquid to paramagnetic state on CeCoGe$_{1-x}$Si$_x$ by means of resonant inverse photoemission spectroscopy (RIPES), which is a very useful method to probe the 4f-electronic structure in unoccupied states. One of the advantages of this technique is a high sensitivity to the variation of the 4f-occupancy, that is, the RIPES effectively detects the dependence of the 4f state on material and temperature. We have measured the RIPE spectra of CeCoGe$_{1-x}$Si$_x$ and found a remarkable reconstruction of the 4f-electronic structure just above the Fermi level $E_F$ with varying composition and temperature.

Measurements were performed in an ultrahigh vacuum chamber where the base pressure is always under 2×10$^{-10}$ Torr. Samples are cooled by a closed cycle 4He refrigerator. Clean sample surfaces were obtained by scraping with a diamond file in a high vacuum every ~60 min at the measurement temperature. A reproducibility of the spectra was checked out at both low and high temperatures. A BaO thermal cathode-type electron gun was used for the excitation source. It was confirmed that it does not give rise to an ascent of sample temperature by the electron-bombardment effect. The kinetic energy of the electron, $E_{ex}$ was calibrated by the electron energy analyzer. The IPE spectra was measured by the soft x-ray emission system which has a Rowland mounted-type spectrometer. The $E_F$ position was determined by referring to the Fermi edge in the IPE spectra of Au which was evaporated on the sample holder. The polycrystalline samples were synthesized by arc melting stoichiometric amounts of the components on a water-cooled copper hearth under a purified argon atmosphere. To improve the homogeneity, the ingot was annealed in an evacuated quartz tube at 950 K for four days followed by an ad-
OBSERVATION OF THE COHERENCE TRANSITION

It is known that the occupancy change in the unoccupied 4f state observed as x increases is caused by the 4f electrons delocalizing by the 4f splitting of the 4f state in the excited state. Here the 4f state is convoluted with the experimental energy resolution of the f i peak. Thus the present f i peak position in this experiment does not exactly show T K. It is thought that the Kondo resonance is located at the lower energy side of the f i peak. However, the relative shift in the f i peak position should provide important information about the shift of T K because the spin-orbit splitting of the 4f state which affects the spectral line shape is not a solid-state effect but an atomic one. The present study on CeCoGe 3−xSi x is thereby a unique test case for which the ground (Kondo) state in the CeCoSi 3 transition is located at the lowest energy position in spite of the highest T K (∼900 K). As discussed later, the f i peak shifts to the higher energy side as temperature increases and coincides with the positions of the other x's. If the ground (Kondo) state in the CeCoSi 3 is attained at 55 K the high spectral intensity at the E F cannot account for the small value of γ(37 mJ/K 2 mole) again. This problem will be mentioned below in the discussion of Fig. 2.

The RIPE spectra of CeCoSi 3 are displayed as a function of temperature up to 285 K in Fig. 2. A continuous and striking reduction of the f i peak has been measured as temperature rises. We define the ratio r f of the f peaks by the following equation as a direct indicator of the 4f occupancy n f:

$$r_f = \frac{I(f^2)}{I(f^1) + I(f^2)}.$$

Here, I(f i) represents the integrated intensities of the f i peak. If the interference of the resonant processes having the f i and f 2 final states is disregarded, r f is equivalent to n f. In a realistic case, however, the configuration interaction in the intermediate and final states of the processes reconstructs the spectra, so that r f does not represent the exact n f. But r f still reflects n f well and is a very useful quantity in the following discussion. The r f's of the several compounds of CeCoGe 3−xSi x are plotted against temperature in Fig. 3(a). The r f's except for x = 3.0 slightly rise with temperature up to 285 K. The relatively constant r f's of x = 1.0 and 0.0 imply that we cross the “coherence line” in a range between x = 1.5 and 1.0 in the T/W vs J phase diagram. The coherence line is associated with a coherence transition from the mixed-valent state of the collective Kondo regime to the paramagnetic state with the local moments in the nonmagnetic region. This is evidence of a scaling behavior of the Kondo resonance by the coherence temperature T coh which will be discussed in more detail by referring to Fig. 3 below. Small variation of the f i peak intensity between x = 0.0 and 1.5 is caused by the stable valency in its paramagnetic state.

conventional annealing at 900 K for ten days. Conventional x-ray examination was carried out on these samples with Cu Kα radiation and the crystal structure has been confirmed to be of the BaNiSn 3 structure type.

Figure 1 shows RIPE spectra of CeCoGe 3−xSi x (x = 0,1,0.5,2,0,3,0) measured at the Ce-N 4,5 absorption edge. The spectra were modified by subtracting the backgrounds. The excitation energy E x = 122.2 eV is selected by referring to the constant-final state spectra of x = 0,0 and 3.0 because the most resonant enhancements of the 4f structures occur approximately at this energy. The peak just above E F is the so-called f i peak and the broad band at around 4 eV is the f 2 peak. The f i peak (n = 1,2) is almost caused by the [4f-c]−→[4f-c] RIPE processes, that is to say, the f i peak reflects the weight of the 4f state in the initial state. Here the c represents the hole in the conduction band. It is known that the f 1 peak structure contains the Kondo resonance located at T K ∼55 K within the framework of the impurity Anderson model. However, in several excited states, the sidebands due to the spin-orbit and crystal-field splitting of the 4f final state are convoluted with the experimental energy resolution of the f i peak. The present f i peak position in this experiment does not exactly show T K. It is thought that the Kondo resonance is located at the lower energy side of the f i peak. However, the relative shift in the f i peak position should provide important information about the shift of T K because the spin-orbit splitting of the 4f state which affects the spectral line shape is not a solid-state effect but an atomic one. The present study on CeCoGe 3−xSi x is thereby a unique test case for which T K can be considerably varied by simply changing the composition x in a single system. The results in Fig. 1 show the changes in the unoccupied 4f state with continuous rise of the J as x increases. The clear reduction of the f i peak is observed as x decreases (the spectral intensities are normalized by the f 2 peak) in Fig. 1. The intensity of the f i peak on CeCoSi 3 is reduced by ∼35% as compared with that of CeCoGe 3. The reduction from x = 3.0 to x = 1.5 is most remarkable. The T K which deduced from the Sommerfeld constant γ of x = 1.5 is reported to be 100 K 2, which is sufficiently higher than the measurement temperature (55 K). It
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The results measured along the lines “A” and “B” are dis- 

saturated in rf below about x = 1.5 along the line “A” is evident in Fig. 3(a). 

Although the clear shift of the f1 peak position to the 

higher energy side with increasing temperature has been put 

into evidence in the present study, the cause for this tempera-

ture dependence is not fully settled at the moment and infor-

mation about the band structure of CeCoGe3−xSi x, or the density of state near Ef around the coherence line would be 

of great importance for our understanding. 

The results of the RIPES of the CeCoGe3−xSi x (0 ≤ x 

≈ 3) have been herein presented as a function of silicon 

concentration x and temperature. First, the f1 peak which is 

associated with the f1 final-state structure just above Ef, 

dramatically grows between x = 1.5 and 3.0 with increasing 

x. This indicates that the localized 4f electron in CeCoGe3 

becomes itinerant due to the enhanced Kondo effect as x 

increases. Second, the f1 peak in the spectra of x = 2.0 and 

3.0 dramatically diminishes as temperature rises above about 

200 K. This fact suggests that a transition from the paramag-

netic state to the coherent Fermi-liquid (mixed-valent) state 

occurs far below the Kondo temperature Tk, so that the 4f 

properties are scaled by the characteristic coherence transi-

tion temperature Tcoh rather than Tk. It should be finally 

remarked that the energy shift of the f1 peak with the com-

position x shown in Fig. 1 does not seem to scale with either 

Tcoh or Tk as the impurity Anderson model predicts. This 

point should be more carefully examined both from experi-

mental and theoretical points of view in the future.

FIG. 3. (a)The f-peak ratio: rf as a function of x plotted against 
temperature T. (b) rf as a function of x plotted against T/Tk. The 
lines on the data are guides for the eyes and a vertical dotted line 
represents the point T = Tk.

reflect the stable 4f-electron numbers nf ~ 1, that is, the 
paramagnetic state with an effective magnetic moment close 
to the value of Ce3+, μeff = 2.54μB. On the other hand, rf 
of x = 3.0, for which the extremely high Tk (of the order of 
900 K) has been reported, shows a dramatic rise from about 
200 to 285 K. As shown by Bickers et al., the transport and 
thermodynamic properties of mixed-valence Ce systems are 
represented by universal functions scaled by Tk in the impurity 

systems. And the scaling behaviors in the high-energy 
spectroscopic results of the several Ce compounds have been 
explained within the impurity model and the Kondo effect 
which dominates the Ce-based heavy fermion systems is 
generally accepted to be well understood in the dilute limit. 

It should be noted, however, that the onset of the rise of the 
rf sets in at a sufficiently lower temperature (~200 K) than 
the single-impurity Tk and the long-range coherence among 
the local singlets seems to be already destroyed at room tem-

terature as indicated in Fig. 3(a). That is, the coherent dense 
Kondo state in CeCoSi3 is strongly suppressed over the 
Tcoh ~200 K. On the other hand, it is apparent from Fig. 
3(b) that rf’s cannot be scaled by the T/Tk contrary to the 
prediction in an impurity approach. This result, we believe, 
gives a direct evidence for the basic energy scaling by Tcoh 
which controls the dense Kondo system. This Tcoh value 
appears to correspond to the temperature where the maxi-

mum value of magnetic susceptibility is found (Tk,max 
= 230 K). The paramagnetic state with localized magnetic 
moments is sustained far below Tk. On the other hand, atten-

tion should be paid to the fact that the Tcoh of 
CeCoSe3−xSi x is much smaller than the single-impurity Tk 
though in the case of CeRu2(Ge1−xSi x)2, the Tcoh is compar-

able to the Tk. This strong material dependence of Tcoh 
suggests that the relationship between Tcoh and Tk is not 
fixed and straightforward even in the spin-fluctuation sys-

tems with a large J.

We interpret our results by a schematic phase diagram as 
shown in Fig. 4, where included are the Neél temperature 
Tn and Weiss temperature θw as a function of x reported by 
Eom et al. The θw is proportional to Tk which exponen-
tially depends on the coupling constant J. We added the co-
herence line Tcoh(x) represented by a thick hatched line. The 
measurements in Figs. 1 and 2 were performed along the 
lines “A” and “B” respectively. It has been found that the 
lines “A” and “B” cross over the coherence line between 
x = 1.0 and 1.5 at around 200 K, respectively. A saturation in 
rf below about x = 1.5 along the line “A” is evident in Fig. 
3(a).

Although the clear shift of the f1 peak position to the 
higher energy side with increasing temperature has been put 
into evidence in the present study, the cause for this tempera-
ture dependence is not fully settled at the moment and infor-
mation about the band structure of CeCoGe3−xSi x, or the density of state near Ef around the coherence line would be 
of great importance for our understanding.

FIG. 4. The schematic phase diagram of the CeCoGe3−xSi x se-

ries. The results measured along the lines “A” and “B” are dis-

played in Figs. 1 and 2, respectively.